

## AMMONIUM OXALATE-CONTAINING POLISHING SYSTEM AND METHOD

### CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

[0001] This patent application claims priority to provisional U.S. Patent Application No. 60/261,928 filed on January 16, 2001.

### TECHNICAL FIELD OF THE INVENTION

[0002] The present invention provides a system and method for polishing or planarizing a substrate, especially a surface comprising a conductive metal.

### BACKGROUND OF THE INVENTION

[0003] Chemical-mechanical polishing (CMP) is a well-known process for planarizing the surfaces of substrates of microelectronic devices, such as semiconductor wafers. CMP typically involves applying a chemically reactive and mechanically abrasive polishing composition or "slurry" to the surface of a substrate. Polishing compositions generally are applied to the surface of a substrate by contacting the surface with a polishing pad saturated with the polishing composition. As the polishing composition chemically reacts with the substrate, the abrasive removes material from the surface of the substrate, thereby polishing the substrate. A more detailed explanation of chemical-mechanical polishing is set forth in U.S. Patents 4,671,851, 4,910,155, and 4,944,836.

[0004] Because planar surfaces optimize the performance of semiconductor wafers, select surfaces of a semiconductor wafer must be polished without adversely affecting underlying structures or topology at a rapid rate and with high selectivity. Compositions that maximize removal rates and selectivity, therefore, are crucial to the efficient fabrication of microelectronic devices.

[0005] Although many CMP compositions and methods are known for improving removal rates and selectivity, such CMP compositions often utilize expensive and environmentally undesirable oxidizing agents. For example, the utilization of an oxidizing agent during the chemical-mechanical polishing of copper is described in U.S. Patent 6,096,652.

[0006] Thus, there exists a need for other polishing systems and methods that improve removal rates and polishing selectivity, while minimizing surface defects and damage to underlying structures or topography, and that do not utilize an oxidizing agent. The invention is directed to providing such a polishing system and method. The advantages of the invention, as well as additional inventive features, will be apparent from the description of the invention provided herein.

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## DETAILED DESCRIPTION OF THE INVENTION

**[0009]** The liquid carrier can be any suitable carrier (e.g., solvent). Suitable liquid carriers include, for example, aqueous carriers (e.g., water) and nonaqueous carriers (e.g., organic liquids). The liquid carrier facilitates the application of other components of the polishing system (e.g., the ammonium oxalate, the hydroxy coupling agent, and, if present and suspended in the liquid carrier, the abrasive) onto the surface of the substrate. Preferably, the liquid carrier is water.

**[0011]** The hydroxy coupling agent can be any suitable hydroxy (-OH) coupling agent. Suitable hydroxy coupling agents, include, for example, coupling agents that can be used to reduce the surface hydroxyl density of metal oxide abrasives. Suitable hydroxy coupling agents that reduce the surface hydroxyl density of metal oxide abrasives include, for example, silane coupling agents, aluminum coupling agents, organotitanium coupling agents, and organophosphorous coupling agents.

**[0012]** The hydroxy coupling agent preferably is a silane-containing compound, such as a silane-containing compound that has the formula  $Y-Si(X_1X_2R)$ , wherein Y, R,  $X_1$ ,

and  $X_2$  individually can be a non-hydrolyzable substituent or a hydrolyzable substituent such as, for example, a hydroxy substituent, so long as at least one of Y, R,  $X_1$ , and  $X_2$  is a hydroxy-containing substituent such that the silane-containing compound is a hydroxy coupling agent. The silane-containing compound can be a dimer, trimer, or oligomer that can contain from about 4 to 15 siloxane units. The silane-containing compound more preferably has the formula  $Y-Si-(X_1X_2R)$ , wherein Y is hydroxy or alkoxy (e.g.,  $C_1-C_{10}$  alkoxy), R is a non-hydrolyzable substituent, and  $X_1$  and  $X_2$  individually are hydrolyzable substituents or, most preferably, non-hydrolyzable substituents. The hydrolyzable substituents generally are those substituents that result in the formation of  $Si(OH)$  in an aqueous medium. Such hydrolyzable substituents include, for example, hydroxy, alkoxy (e.g.,  $C_1-C_{10}$  alkoxy), halogen such as chloride, carboxylate, and amide. The non-hydrolyzable substituents generally are those that do not result in the formation of  $Si(OH)$  in an aqueous medium. Such non-hydrolyzable substituents include, for example, alkyl (e.g.,  $C_1-C_{25}$  alkyl), alkene (e.g.,  $C_2-C_{25}$  alkene), and aryl (e.g.,  $C_6-C_{25}$  aryl), any of which can be in any configuration, functionalized, and substituted with any suitable atom, such as oxygen, nitrogen, sulfur, phosphorous, halogen, silicon, and combinations thereof. Preferably, the non-hydrolyzable substituent is a functionalized alkyl (e.g., a  $C_1-C_{25}$  alkyl) selected from the group consisting of alkyl nitrile, alkyl amide, alkyl carboxylic acid, or alkyl ureido. The silane-containing compound most preferably has the formula  $Y-Si-(X_1X_2R)$ , wherein Y,  $X_1$ , and  $X_2$  individually are hydroxy or  $C_1-C_{10}$  alkoxy, and R is a ureido( $C_1-C_{10}$ )alkyl.

**[0013]** Suitable silane-containing hydroxy coupling agents include, for example, aminosilanes, ureidosilanes, alkoxysilanes, alkylsilanes, mercaptosilanes, vinylsilanes, cyanosilanes, thiocyanatosilanes, functionalized silanes, disilanes, trisilanes, and combinations thereof. Silanes with a single hydrolyzable substituent include, for example, cyanopropyl dimethylalkoxysilane,  $N,N'$ -(alkoxymethylsilylene)bis[N-methyl-benzamide], chloromethyl dimethylalkoxysilane, and mixtures thereof. Silanes with two hydrolyzable substituents include, for example, chloropropyl methyl dialkoxysilane, 1,2-ethanediylbis[alkoxydimethyl] silane, dialkoxymethylphenyl silane, and mixtures thereof. Suitable silanes with three hydrolyzable substituents include, for example, glycidoxypropyl trialkoxysilane, isocyanatopropyl trialkoxysilane, ureidopropyl trialkoxysilane, mercaptopropyl trialkoxysilane, cyanoethyl trialkoxysilane, 4,5-dihydro-1-(3-trialkoxysilylpropyl)imidazole, 3-(trialkoxysilyl)-methyl ester propanoic acid, trialkoxy[3-(oxiranylalkoxy)propyl]-silane, 2-methyl, 3-(trialkoxysilyl)propyl ester 2-propenoic acid, [3-(trialkoxysilyl)propyl] urea, and mixtures thereof. Most preferably, the hydroxy coupling agent is ureidopropyl trimethoxysilane, especially gamma-ureidopropyl trimethoxysilane.

[0014] The hydroxy coupling agent is present in the polishing system in any suitable amount. Preferably, the hydroxy coupling agent is present in the liquid portion of the polishing system in an amount of about 0.01-1 wt.%. More preferably, the hydroxy-coupling agent is present in the liquid portion of the polishing system in an amount of about 0.01-0.1 wt.%.

[0015] Any suitable polishing pad can be used in the polishing system. The polishing pad can be any suitable abrasive or non-abrasive pad. Moreover, the polishing system can comprise a polishing pad (either an abrasive pad or a non-abrasive pad), wherein either an abrasive is suspended in the liquid portion of the polishing system or no abrasive is suspended in the liquid portion of the polishing system. Suitable polishing pads are described, for example, in U.S. Patents 5,849,051 and 5,849,052. Suitable polishing pads include, for example, woven and non-woven polishing pads. Moreover, suitable polishing pads can comprise any suitable polymer of varying density, hardness, thickness, compressibility, ability to rebound upon compression, and compression modulus. Suitable polymers include, for example, polyvinylchlorides, polyvinylfluorides, nylons, fluorocarbons, polycarbonates, polyesters, polyacrylates, polyethers, polyethylenes, polyurethanes, polystyrenes, polypropylenes, polymelamines, polyamides, polyvinyl acetates, polyacrylic acids, polyacrylamides, polysulfones, and coformed products thereof, and mixtures thereof. When an abrasive is fixed (e.g., embedded), in whole or in part, in or on the polishing pad of the polishing system, such fixation on the polishing pad can be accomplished in any suitable manner.

[0016] The polishing system can comprise any suitable abrasive. The abrasive can be suspended in the liquid carrier (e.g., water) of the polishing system, thereby being a part of the liquid portion of the polishing system. The abrasive of the polishing system can be fixed (e.g., embedded), in whole or in part, in or on a polishing pad (e.g. polishing surface).

[0017] The abrasive of the polishing system can be any suitable abrasive. The abrasive can be heat-treated and/or chemically-treated (e.g., an abrasive with chemically-linked organic functional groups). Suitable abrasives include, for example, metal oxides. Suitable metal oxides include, for example, alumina, silica, titania, ceria, zirconia, germania, magnesia, and coformed products thereof, and mixtures thereof. The metal oxides can be fumed (i.e., pyrogenic), precipitated, condensation-polymerized, or colloidal in nature. For example, the metal oxides can be as described in U.S. Patent 5,230,833 or the commercially available Akzo-Nobel Bindzil 50/80 or Nalco 1050, 2327, or 2329 metal oxide particles, as well as other similar products available from DuPont, Bayer, Applied Research, Nissan Chemical, and Clariant. The abrasive of the polishing system preferably is a fumed metal oxide. More preferably, the abrasive is fumed silica.

[0018] The abrasive can be present in the polishing system in any suitable amount. For example, the abrasive can be present in the liquid portion of the polishing system in an amount of about 0.1-20 wt.%. Preferably, the abrasive is present in the liquid portion of the polishing system in an amount of about 0.1-10 wt.%. More preferably, the abrasive is present in the liquid portion of the polishing system in an amount of about 0.1-1 wt.% (e.g., about 0.2-0.8 wt.%).

[0019] The polishing system optionally comprises a film-forming agent. The film-forming agent can be any suitable film-forming agent. Suitable film-forming agents include, for example, any compound, or mixture of compounds, that facilitates the formation of a passivation layer (i.e., a dissolution-inhibiting layer) on a metal layer and/or a metal oxide layer. Suitable film-forming agents include, for example, nitrogen-containing heterocyclic compounds. Preferably, the film-forming agent comprises one or more 5-6 member heterocyclic nitrogen-containing rings. More preferably, the film-forming agent is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, benzotriazole, benzimidazole, benzothiazole, and derivatives thereof, such as, for example, hydroxy-, amino-, imino-, carboxy-, mercapto-, nitro-, urea-, thiourea-, or alkyl-substituted derivatives thereof. Most preferably, the film-forming agent is benzotriazole.

[0020] The film-forming agent can be present in the polishing system in any suitable amount. Preferably, the film-forming agent is present in the liquid portion of the polishing system in an amount of about 0.005-1 wt.%. More preferably, the film-forming agent is present in the liquid portion of the polishing system in an amount of about 0.01-0.2 wt.%.

[0021] The polishing system can have any suitable pH. The pH of the polishing system desirably is about 7-13. Preferably, the polishing system has a pH of about 8-12. More preferably, the pH of the polishing system is about 9-11.

[0022] Any suitable pH adjusting agent can be used to adjust the pH of the polishing system. Suitable pH adjusting agents include, for example, acids and bases. Typically, the polishing system will include a base, such as a hydroxide compound, e.g., potassium hydroxide, sodium hydroxide, ammonium hydroxide, lithium hydroxide, magnesium hydroxide, calcium hydroxide, or barium hydroxide, or an amine compound. The pH adjusting agent can be a mixture of compounds, such as a mixture of potassium hydroxide and lithium hydroxide. The pH adjusting agent can be in the form of a solution, e.g., an aqueous solution. An example of a metal hydroxide-containing solution that can be a pH adjusting agent is a solution of potassium hydroxide in deionized or distilled water in which the amount of potassium hydroxide is about 0.1-0.5 wt.% (e.g., about 0.2-0.3 wt.%). Preferably, the pH adjusting agent is potassium hydroxide.

[0023] Other components can be, but need not be, present in the polishing system. Such other components can be compounds that stabilize the polishing system or that

improve or enhance the performance of the polishing system. For example, buffers can be present in the polishing system. Suitable buffers include carbonates (e.g., potassium carbonate), phosphates, and carboxylic acids. Desirably, the polishing system does not contain an oxidizing agent.

[0024] The polishing system preferably has a polishing selectivity of copper to tantalum (i.e., a Cu:Ta removal rate) of at least about 1:1, such as at least about 2:1. The polishing system preferably has a polishing selectivity of copper to tetraethoxysilane (TEOS) (i.e., a Cu:TEOS removal rate) of at least about 1:2.

[0025] The invention also provides a method of polishing or planarizing a substrate comprising contacting at least a portion of a substrate with the polishing system and polishing the portion of the substrate therewith. The polishing system can be used to polish any suitable substrate, especially one or more layers of a multi-layer substrate. Preferably, the polishing system is used to polish a multi-layer substrate that includes a first metal layer, a second layer, and optionally one or more additional layers. Suitable first metal layers include, for example, copper (Cu), aluminum (Al), aluminum copper (Al-Cu), aluminum silicon (Al-Si), titanium (Ti), titanium nitride (TiN), tungsten (W), tungsten nitride (WN), noble metals (e.g., iridium (Ir), ruthenium (Ru), gold (Au), silver (Ag), and platinum (Pt)), and combinations thereof. Suitable second layers include, for example, titanium (Ti), titanium nitride (TiN), tantalum (Ta), tantalum nitride (TaN), tungsten (W), tungsten nitride (WN), oxides (e.g., silicon dioxide), low- $\kappa$  materials and dielectrics (e.g., porous silica, fluorine-doped glass, carbon-doped glass, and organic polymers), and combinations thereof. Most preferably, the substrate comprises a first metal layer of copper or a copper alloy (i.e., a combination of copper and one or more metals), an adhesive layer of tantalum (Ta) or tantalum nitride (TaN), and a layer of tetraethoxysilane (TEOS).

[0026] In addition to being suitable for polishing semiconductor wafers, the polishing system can be used to polish or planarize other substrates, such as prime silicon, rigid or memory disks, inter-layer dielectrics (ILDs), micro-electromechanical systems (MEMS), ferroelectrics, magnetic heads, noble metals, polymeric films, and low and high dielectric constant films.

#### EXAMPLE

[0027] This example further illustrates the present invention but, of course, should not be construed as in any way limiting its scope. This example illustrates the improved performance that can be achieved through use of the polishing system and method of the invention, particularly to provide an increased copper removal rate in polishing a copper-containing multi-component substrate.

**[0028]** Nine polishing systems (A – I) were prepared, each of which contained about 0.6 wt.% fumed silica (Cabot's Cab-O-Sil® L-90 fumed silica), about 0.25 wt.% gamma-ureidopropyltrimethoxysilane, about 0.04 wt.% benzotriazole, about 0.03 wt.% potassium hydroxide, about 0.004 wt.% potassium carbonate, water, and either no polishing additive (polishing system A) or 1 wt.% of a polishing additive (polishing systems B – I). The polishing additive was different in each polishing system and was either tartaric acid (polishing system B), N-acetyl glycine (polishing system C), potassium oxalate (polishing system D), aminotri(methylenephosphonic acid) (polishing system E), ammonium sulfate (polishing system F), ammonium acetate (polishing system G), diammonium EDTA (polishing system H), or ammonium oxalate (polishing system I). Thus, this example involved a control polishing system (A), comparative polishing systems (B – I), and the polishing system of the invention (I). Each of these polishing systems was used to polish a similar semiconductor wafer comprising copper, tantalum, and TEOS under similar conditions. The rate at which the copper on the substrate was removed was determined for each polishing system.

**[0029]** The substrates were polished with the polishing systems on an IPEC 472 polishing device using a Rodel® IC1000 pad. The substrates were subjected to a downforce pressure of about 20 kPa (3 psi), a platen speed of 87 rpm, and a carrier speed of 93 rpm. The polishing systems were supplied to the polishing device at a rate of 180-200 ml/ min for 60 sec. Following the use of the polishing systems, the removal rates of copper from the substrates were measured. The resulting data is set forth in the following table.

Table: Copper Removal Rates

Polishing System	Polishing Additive	Copper Removal Rate [Å/min]
A	none	270
B	tartaric acid	291
C	N-acetyl glycine	263
D	potassium oxalate	227
E	aminotri(methylenephosphonic acid)	247
F	ammonium sulfate	234
G	ammonium acetate	227
H	diammonium EDTA	260
I	ammonium oxalate	673

[0030] As is apparent from the data set forth in the table, the polishing system of the invention (i.e., polishing system I) that contained ammonium oxalate achieved a much higher copper removal rate than the control and comparative polishing systems (i.e., polishing systems A – H) that did not contain ammonium oxalate but were otherwise similar to the polishing system of the invention. In particular, the utilization of ammonium oxalate in conjunction with a liquid carrier, a hydroxy coupling agent, and a polishing pad and/or an abrasive increased the copper removal rate by a factor of about 2-3, as compared to similar polishing systems that did not contain ammonium oxalate.

[0031] All of the references cited herein, including patents, patent applications, and publications, are hereby incorporated in their entireties by reference.

[0032] While this invention has been described with an emphasis upon preferred embodiments, variations of the preferred embodiments may be used, and it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the claims.